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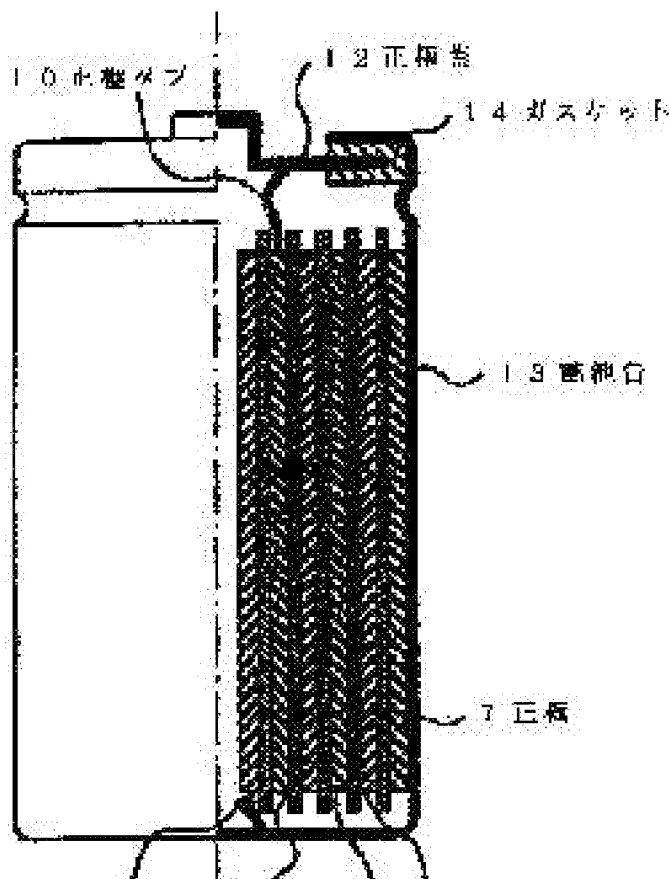
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(54) COMPOSITE CARBON PARTICLE, ITS PRODUCTION, NEGATIVE POLE MATERIAL, NEGATIVE POLE FOR LITHIUM SECONDARY BATTERY OR CELL AND LITHIUM SECONDARY BATTERY OR CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To produce a composite carbon particle which is a high graphitic carbon, maintaining characteristics such as a high charge discharge capacity and low reactivity with an electrolyte, scarce production of dendritic metallic lithium and a high and flat discharge voltage and suitable as a negative pole material for a lithium secondary battery or cell excellent in cycle characteristics and having a small irreversible capacity, to provide a method for producing the composite carbon particle, to obtain the negative pole material and to provide both the negative pole for the lithium secondary battery or cell and the lithium secondary battery or cell.

SOLUTION: This composite carbon particle contains a graphite part, an amorphous carbon part and silicon. The method for producing the composite carbon particle comprises mixing a graphitic particle with an



organosilicon compound and a carbon precursor, heating the resultant mixture and decomposing and carbonizing the organosilicon compound and carbon precursor. The



negative pole material contains the above composite carbon particle or the composite carbon particle obtained by the above method for production. The negative pole for the lithium secondary battery or cell uses the negative pole material. The lithium secondary battery or cell has the negative pole for the lithium secondary battery or cell.

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CLAIMS

[Claim(s)]

[Claim 1]A compound carbon particle containing a black lead portion, an amorphous carbon portion, and silicon.

[Claim 2]The compound carbon particle according to claim 1 which has the structure which a graphite-grains child covered with amorphous carbon which includes silicon condensed.

[Claim 3]A silicon content measured by X-ray fluorescence is 1 to 20 % of the weight, and specific surface area Below 10-m²/g. The compound carbon particle according to claim 1 or 2 whose spacings of a field (002) originating in a black lead portion and an amorphous carbon portion which are measured by a wide angle X diffraction are less than 0.336 nm and 0.340 nm or more, respectively.

[Claim 4]A manufacturing method of a compound carbon particle mixing and heating graphite particles with an organosilicon compound and a carbon precursor, and disassembling and carbonizing an organosilicon compound and a carbon precursor.

[Claim 5]A manufacturing method of the compound carbon particle according to claim 4 which graphite particles are graphite particles which flat shape particles gather or combine with non parallel mutually, and is what has fine pores of 0.4 - 2.0 cc/g in the range of 0.1-100 micrometers.

[Claim 6]A manufacturing method of the compound carbon particle according to claim 4 or 5 whose organosilicon compound is a silicon alkoxide or its partial condensation polymer.

[Claim 7]A manufacturing method of the compound carbon particle according to claim 4, 5, or 6 which makes disassembly of an organosilicon compound and a carbon precursor, and carbonization temperature 900-1400 **.

[Claim 8]A negative pole material containing a compound carbon particle obtained by claims 1 and 2, compound carbon particle given in 3, claims 4, 5, and 6, or a manufacturing method given in 7.

[Claim 9]A negative electrode for lithium secondary batteries which uses the negative pole material according to claim 8.

[Claim 10]A lithium secondary battery which has the negative electrode for lithium secondary batteries according to claim 9.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the suitable compound carbon particle for the lithium secondary battery excellent in especially charge-and-discharge capacity and a cycle characteristic, its negative electrode, a negative pole material, and said negative pole material, and its manufacturing method about the suitable compound carbon particle for a lithium secondary battery, its negative electrode, a negative pole material, and said negative pole material, and its manufacturing method.

[0002]

[Description of the Prior Art]In recent years, the requests to small size and the rechargeable battery which is lightweight and has high energy density are mounting as a portable device, an electromobile, and an object for stationary energy storage. The nonaqueous electrolytic solution secondary battery, especially the rechargeable lithium-ion battery attract attention to such a request as cells which especially have high tension and high energy density.

[0003]As a negative pole material of a rechargeable lithium-ion battery, metal lithium, amorphous carbon particles, and high graphitized carbon particles are used. Although metal lithium can realize high charge-and-discharge capacity, Moreover it reacts to the solvent in an electrolysis solution with progress of a charging and discharging cycle for [the] high reactivity and capacity falls, it is easy to generate metal lithium of arborescence, and the separator formed between right and a negative electrode is penetrated, and it has the problem of being easy to cause a short circuit.

[0004]Although it has the feature that arborescence metal lithium with low reactivity with an electrolysis solution is hard to generate the nature material of amorphous carbon, since true density is low, generally charge-and-discharge capacity has low the difficulty that the charge-and-discharge capacity per volume is low. High graphitized carbon particles have high charge-and-discharge capacity as compared with amorphous carbon particles, Since it has the feature reactivity with an electrolysis solution is low as compared with metal lithium, and arborescence metal lithium is hard to generate that discharge voltage is high and flat, it succeeds in examination increasingly briskly as a charge of negative-electrode material in recent years.

[0005]However, the service capacity of high graphitized carbon has the technical problem that it is restricted by lithium and the intercalation compound (LiC_6) to form (372 mAh/g). Although development of the charge of a high graphitized carbon material which has the capacity exceeding this

theoretical capacity is considered, what was compatible in workability and a cycle characteristic is not yet found out.

[0006]Although acid carbide, such as a tin content oxide, a silicon oxide, silicon, aluminum, and tungsten, etc. are proposed and it is reported as except the above-mentioned negative pole material that high service capacity is chosen, there is a technical problem in a cycle characteristic, irreversible capacity, etc., and there is nothing that is still put in practical use.

[0007]

[Problem(s) to be Solved by the Invention]This invention with low reactivity with the high charge-and-discharge capacity of high graphite carbon, and an electrolysis solution. The feature arborescence metal lithium is hard to generate that discharge voltage is high and flat is maintained, it excels in a cycle characteristic, and a compound carbon particle suitable as a negative pole material for lithium secondary batteries with small irreversible capacity is provided.

[0008]This invention with low reactivity with the high charge-and-discharge capacity of high graphite carbon, and an electrolysis solution. The feature arborescence metal lithium is hard to generate that discharge voltage is high and flat is maintained, it excels in a cycle characteristic, and the manufacturing method of a compound carbon particle suitable as a negative pole material for lithium secondary batteries with small irreversible capacity is provided.

[0009]This invention provides the suitable negative pole material for the lithium secondary batteries with small irreversible capacity which maintained the feature arborescence metal lithium with low reactivity with the high charge-and-discharge capacity of high graphite carbon and an electrolysis solution is hard to generate that discharge voltage is high and flat, and were excellent in the cycle characteristic.

[0010]This invention provides the negative electrode for lithium secondary batteries with small irreversible capacity arborescence metal lithium with low reactivity with high charge-and-discharge capacity and an electrolysis solution is hard to generate and which has the feature that discharge voltage is high and flat, and was excellent in the cycle characteristic. This invention has high service capacity, is excellent in a cycle characteristic, and provides a lithium secondary battery with small irreversible capacity.

[0011]

[Means for Solving the Problem]This invention relates to a compound carbon particle containing a black lead portion, an amorphous carbon portion, and silicon. This invention relates to said compound carbon particle which has the structure which a graphite-grains child covered with amorphous carbon which includes silicon condensed. A silicon content by which this invention is measured by X-ray fluorescence is 1 to 20 % of the weight, A spacing of a field (002) where specific surface area originates in a black lead portion and an amorphous carbon portion which are measured by a wide angle X diffraction below as for $10\text{-m}^2/\text{g}$ is related with said compound carbon particle which are less than 0.336 nm and 0.340 nm or more, respectively.

[0012]This invention relates to a manufacturing method of a compound carbon particle mixing and heating graphite particles with an organosilicon compound and a carbon precursor, and disassembling and carbonizing an organosilicon compound and a carbon precursor. Said graphite particles are graphite particles which flat shape particles gather or combine with non parallel mutually, and this invention relates to a manufacturing method of a compound carbon particle which is what has fine pores of 0.4 - 2.0 cc/g in the range of 0.1-100 micrometers. This invention relates to a manufacturing method of a

compound carbon particle in which said organosilicon compound is a silicon alkoxide or its partial condensation polymer. This invention relates to a manufacturing method of a compound carbon particle which makes disassembly of said organosilicon compound and a carbon precursor, and carbonization temperature 900-1400 **.

[0013] This invention relates to a negative pole material containing a compound carbon particle obtained by a compound carbon particle or the aforementioned manufacturing method given in above any they are. This invention relates to a negative electrode for lithium secondary batteries which uses the aforementioned negative pole material. This invention relates to a lithium secondary battery which has the aforementioned negative electrode for lithium secondary batteries.

[0014]

[Embodiment of the Invention] The compound carbon particle of this invention contains a black lead portion, an amorphous carbon portion, and silicon. Here, composite means that a black lead portion and an amorphous carbon portion unify, and are contained in the composite particle piece instead of the mixture of graphite particles and a carbonaceous particle, and silicon is contained in this composite particle. In the composition of the state of the mixture of other composition, i.e., graphite particles, a carbonaceous particle, the state of the mixture of silicon content particles and graphite particles, and the carbonaceous particle containing silicon, etc., the high service capacity and cycle characteristic like this invention are not realized.

[0015] Although restriction in particular is not carried out about the rate of the black lead portion contained in a compound carbon particle, and its particle number, it is preferred to contain two or more graphite-grains children in 1 composite particle at the point of raising a cycle characteristic. It can check, for example that silicon contains in the compound carbon particle of this invention by conducting X-ray fluorescence of the composite particle. Although there is no restriction in particular about the existence state of silicon, the state, i.e., the thing which exists as amorphous compounds, where the clear diffraction line which corresponds to a silicon content compound in the wide angle X diffraction figure of a composite particle is not accepted is preferred.

[0016] In the wide angle X diffraction of the compound carbon particle of this invention, it is preferred that a diffraction line of 0.336 nm or less is accepted for the spacing d of a field (002). Such a diffraction line originates in the black lead portion (graphite particles) which constitutes a compound carbon particle, and can be attained by using the graphite particles which graphitization followed. It is in the tendency for a cycle characteristic to fall, in some in which the diffraction line with which this spacing d exceeds 0.336 nm appears.

[0017] In the wide angle X diffraction of the compound carbon particle of this invention, it is preferred that a diffraction line of 0.340 nm or more is observed for the spacing d of a field (002). Such a diffraction line originates in the amorphous carbon which constitutes a composite particle. The carbon in which the diffraction line below 0.340 nm appears has the remarkable tendency to be a case where it carbonizes at an elevated temperature, for silicon which is another essential ingredient of this invention at such an elevated temperature to silicon-carbide-ize, and for service capacity to fall.

[0018] Amorphous carbon as used in the field of this invention is also called amorphous carbon, and refers to low-level carbon of development of a crystal, A low-temperature-treatment article (what has L_c and L_a large d_{002} and small) and difficulty graphitized carbon which does not turn into high graphitized carbon even if it carries out high temperature processing of easily graphitized carbon which are called low graphitized carbon and which will turn into high graphite if high temperature processing is carried

out are included.

[0019]The compound carbon particle of this invention mixes graphite particles with an organosilicon compound and a carbon precursor, with heating, can disassemble and carbonize an organosilicon compound and a carbon precursor, respectively, and can create them. In this way, the compound carbon particle obtained has the structure which the graphite particles covered with the amorphous carbon which includes silicon condensed. As for the graphite particles to be used, although the grinding thing of natural graphite, an artificial graphite, and expanded graphite, etc. are mentioned, it is preferred that the impurity to contain uses the thing of a high grade of 2000 ppm or less. When graphite particles with a large impurity content are used, it is in the tendency for a cycle characteristic to deteriorate.

[0020]As for the graphite particles used by this invention, it is preferred that they are the graphite particles which flat shape particles gather or combine with non parallel mutually, The effect that that whose pore volume of the range of 0.001-100 micrometers measured with a method of mercury penetration is 0.4 or more cc/g raises a cycle characteristic is highly preferred. Such particles incorporate an organosilicon compound and a carbon precursor organic polymer compound in fine pores, In order for silicon and carbon to come to exist not only in a graphite particle outermost surface but in its inside as the result and to equalize the stress at the time of a charging and discharging cycle, it is thought that a cycle characteristic improves. Here, when said pore volume uses the small graphite particles of less than 0.4 cc/g, the improvement effect of a cycle characteristic is small.

[0021]The aforementioned flat shape particles are particles of shape which have a major axis and a minor axis, and a perfect not spherical thing is said. For example, the thing of shape, such as a lepidic form, the shape of a scale, and massive [a part of], is contained in this. In the particles of two or more flat shape, the field and the state where it has gathered without two or more particles gathering each orientation surface in the fixed direction by using a near field as an orientation surface most level if it puts in another way which carried out flat where an orientation surface has non parallel in the shape of each particle are said. If the state where particles with a mutual combination have pasted up via the binder etc. is said although the particles of flat shape are gathered or combined, and particles with a mutual set paste up with a binder etc., there is nothing, but it originates in the shape and the state where the shape as the aggregate is maintained is said. From the field of mechanical intensity, a united thing is preferred. As a size of each flat particle, it is preferred that it is 0.1-30 micrometers in mean particle diameter, and it is preferred that it is 1/10 or less [of a graphite-grains child's mean particle diameter which these gathered or combined]. In this invention, mean particle diameter can be measured with a laser diffraction particle-size-distribution meter.

[0022]Although there is no restriction in particular and organic silicon polymer, such as polysilane and polysilazane, a silicon alkoxide, its derivative, its partial condensation polymer, etc. can be used as an organosilicon compound used with the manufacturing method of this invention, It is preferred to use the silicon alkoxide which also gives the characteristic cheaply available in respect of a manufacturing cost and good, or its partial condensation polymer. As a silicon alkoxide, a tetramethoxy silane, a tetraethoxysilane, Alkoxy groups, such as tetra propoxysilane, trimethoxy methylsilane, and TORIETOKISHI methylsilane, can combine with 1-4-piece silicon, and it can use as what has a desirable thing whose remainder is a hydrocarbon group. Generally, under acid catalyst existence, condensation polymerization is carried out, it is produced and the partial condensation polymer can use [partial hydrolysis and] the partial condensation polymer of a tetramethoxy silane and a tetraethoxysilane for the above-mentioned silicon alkoxide.

[0023]As a carbon precursor used with the manufacturing method of this invention, They are mentioned by various organic polymer compounds and For example, a petroleum system pitch, a Carboniferous system pitch, Acrylic resins, such as a resultant pitch, tar, polyvinyl chloride, a polyvinylidene chloride, phenol resin, polyacrylonitrile, and poly (alpha-halogenation acrylonitrile), polyamide imide resin, polyamide resin, polyimide resin, etc. can be used.

[0024]Although not restricted in particular about a mixing method with graphite particles, an organosilicon compound, and a carbon precursor, in order to produce the compound carbon particle which is excellent in the characteristic, it is preferred to make these compounds apply and permeate uniformly the surface (if it is in the graphite particles which have fine pores, it is to the inside of fine pores) of graphite particles. Graphite particles, an organosilicon compound, and the uniform mixture of a carbon precursor can be obtained by using an organosilicon compound and a carbon precursor organic polymer compound as a solution, for example, using a solvent as a method of realizing this, distributing graphite particles in this solution, mixing in it, and subsequently removing a solvent.

[0025]Both the solvents to be used can be especially used without restriction, if an organosilicon compound and a carbon precursor can be dissolved. For example, when using a pitch and tar as a carbon precursor, quinoline, pyridine, toluene, benzene, a tetrahydrofuran, creosote oil, etc. can be used, and when using polyvinyl chloride, a tetrahydrofuran, cyclohexanone, nitrobenzene, etc. can be used.

[0026]As the mixing ratio of graphite particles, an organosilicon compound, and a carbon precursor, it is preferred to consider it as 40 to 90 % of the weight of graphite particles, 5 to 30 % of the weight of organosilicon compounds, and 5 to 30 % of the weight of carbon precursors.

[0027]As for the obtained graphite particles, an organosilicon compound, and the mixture of a carbon precursor, it is preferred to grind in advance of the following heating process. A publicly known mechanically ground device can be used for this grinding. Classifying processing may be performed using classifiers, such as a wind force type and a mechanical cable type.

[0028]It ranks second, the obtained graphite particles, an organosilicon compound, and the mixture of a carbon precursor are heated, and an organosilicon compound and a carbon precursor are disassembled and carbonized, respectively. As for the temperature of carbonization here, it is preferred to consider it as 900-1400 **. If carbonization temperature is in the tendency for irreversible capacity to become large at less than 900 ** and carbonization temperature exceeds 1400 ** on the other hand, A reaction with an organosilicon compound decomposition product, carbon and/, or graphite particles occurs violently, and when the diffraction line of silicon carbide comes to be observed in a wide angle X diffraction figure and it uses for it as a negative pole material, service capacity is in the tendency to fall remarkably. As an atmosphere in the case of carbonization, a nitrogen atmosphere, an inert atmosphere, a vacuum atmosphere, etc. can be used. The obtained composite can be cracked and also classified using a publicly known mechanically ground device.

[0029]As for the volume mean particle diameter of the compound carbon particle obtained, it is preferred to consider it as the range of 1-60 micrometers. If mean particle diameter exceeds 60 micrometers, when it will become easy to generate unevenness in an electrode surface and mean particle diameter will be less than 1 micrometer on the other hand, it is in the tendency for irreversible capacity to become large.

[0030]As for the silicon content in the compound carbon particle obtained, it is preferred to consider it as 1 to 20 % of the weight in X-ray fluorescence. Here, in less than 1 % of the weight, there are few addition effects, and when it exceeds 20 % of the weight, there is a tendency for irreversible capacity to

become large.

[0031]As for the specific surface area of the compound carbon particle obtained, it is preferred that below $10\text{-m}^2/\text{g}$ carries out, and it is more preferred that below $5\text{-m}^2/\text{g}$ carries out. Although a minimum in particular is not restricted, it is preferred that it is more than $1\text{-m}^2/\text{g}$. Specific surface area is the value measured in accordance with the BET adsorption method using nitrogen gas with liquid nitrogen boiling point temperature here. It is in the tendency which is one of the tendencies for irreversible capacity to become large, and is inferior in the workability at the time of electrode production in the compound carbon particle in which specific surface area exceeds $10\text{-m}^2/\text{g}$.

[0032]Thus, the compound carbon particle obtained can be used as a negative pole material of a lithium secondary battery. The negative pole material of this invention can be used as the negative-electrode Plastic solid for lithium secondary batteries as follows, for example.

[0033]For example, it kneads with an organic high polymer binder, is made paste state, and can fabricate in shape, such as a sheet shaped. As an organic high polymer binder, polyethylene, polypropylene, polyethylene terephthalate, Aromatic polyamide, aromatic polyimide, cellulose, polyvinylidene fluoride, Polymer materials, such as copolymerization fluorine polymer containing polytetrafluoroethylene and tetrafluoroethylene, Rubber-like polymer materials, such as styrene-butadiene rubber, polyisoprene rubber, butadiene rubber, and ethylene-propylene rubber, Elasticity polymer materials, such as an ethylene-vinyl acetate copolymer, propylene, an alpha olefin copolymer, Polyethylene oxide, polypropylene oxide, polyepichlorohydrin, Ion conductivity polymer materials, such as a system which composite-ized alkali metal salt which makes lithium salt or lithium a subject, can be used for charges of an organic high polymer material, such as poly FAZEN, polyvinylidene fluoride, and polyacrylonitrile.

[0034]Carboxymethyl cellulose, sodium polyacrylate, other acrylic polymer, etc. other than these organic high polymer binders may be added as a viscosity controlling agent. An organic high polymer binder has 0.1 to 30 preferred weight section to negative pole material 100 weight section, the mixing ratio of these organic high polymer binders and negative pole materials of this invention has 0.5 to 20 more preferred weight section, and its one to 15 weight section is still more preferred.

[0035]The negative pole material of this invention can be mixed with the above-mentioned organic high polymer binder, it can fabricate by methods, such as roll forming and compression molding, in the shape of an electrode as it is, and a negative-electrode Plastic solid can be produced. The powder of the negative pole material of this invention and the mixture of the above-mentioned organic high polymer binder may be distributed in a solvent, it may be considered as a slurry, and this may be applied to metal charge collectors etc. As charge collector metal, rolled copper foil, electrolytic copper foil, punching copper foil, nickel foil, etc. are used. A sheet shaped, a pellet type, etc. can set up the shape of an electrode Plastic solid arbitrarily.

[0036]As said solvent, there is no restriction in particular, N-methyl-2-pyrrolidone, dimethylformamide, isopropanol, etc. are raised, and there is no restriction in particular in the quantity. Although a cell is assembled using the negative electrode produced by making it above, a negative-electrode Plastic solid can be made to support the lithium metal which is an active material in advance of this in the case of an assembly. Thereby, the irreversible capacity at the time of first time charge can decrease substantially. These support methods include the chemical method, a physical method, and an electrochemical process, For example, a negative-electrode Plastic solid is immersed in a lithium ion content electrolysis solution, and there are the method of using metal lithium for a counter electrode and carrying out electric being impregnated, a method of mixing metal lithium powder at the time of negative-electrode Plastic

solid production, a method of contacting electrically metal lithium and a negative-electrode pole Plastic solid, etc.

[0037]Via a separator, the negative electrode for lithium secondary batteries produced as mentioned above counters with an anode, is arranged, and constitutes a lithium secondary battery. Especially as a positive electrode material, although not limited, for example A vanadium oxide, a vanadic sulfide, A molybdenum oxide, a molybdenum sulfide, a manganic acid ghost, a manganese sulfide, A chromium oxidation thing, titanium oxide, titanium sulfides, these multiple oxides, Metal chalcogen compounds, such as multiple sulfides, a lithium cobalt oxide (LiCoO_2), a lithium nickel oxide (LiNiO_2) and a lithium manganic acid ghost ($\text{LiMn}_2\text{O}_{--}$) [4 and] Multiple oxides, such as LiMnO_3 and a lithium nickel cobalt oxide ($\text{Li}_x\text{nickel}_y\text{Co}_{(1-y)}\text{O}_2$), the multiple oxide which added other metallic elements (aluminum, Fe, Mn, Mg, Co, etc.) to these, etc. can be used. Conductive polymers, such as poly aniline and polypyrrole, can also be used.

[0038]As an electrolysis solution, what dissolved lithium salt used as an electrolyte in the nonaqueous solvent is used. As an electrolyte, LiClO_4 , LiPF_6 , LiAsF_6 , Lithium metal salts, such as LiBF_4 , LiSO_3CF_3 , and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, tetra-alkyl ammonium salt, etc. can be used. As for the concentration of lithium salt, 1. is preferred in 0.2-2 mol /, and it is 0.3-1.9 mol/l. more preferably.

[0039]As a nonaqueous solvent, propylene carbonate, ethylene carbonate, Cyclic ester, such as butylene carbonate, vinylene carbonate, and gamma-butyrolactone. Ether, such as ketone, such as chain ester species, such as diethyl carbonate, and methyl ethyl ketone, 1,2-dimethoxyethane, dioxolane, a tetrahydrofuran, a 1,2-dimethyltetrahydrofuran, and crown ether, can be used. The solid electrolyte mixed by polyethylene oxide, polyphosphazene, a polyaziridine, polyacrylonitrile, polyethylene sulfides, etc. these derivatives, the mixture, the complex, etc. in the above-mentioned salts can also be used. In this case, the solid electrolyte can serve also as a separator and a separator becomes unnecessary. A negative electrode and an anode can be separated and fine porous films, such as polyethylene, polypropylene, polypropylene / polypropylene multicomputer system, polypropylene / fluoro-resin multicomputer system, a nonwoven fabric, etc. can be used as a separator holding an electrolysis solution.

[0040]

[Example]Hereafter, this invention is explained using an example.

The tetramethoxy silane partial condensation polymer (trade name M-silicate, Tama Chemicals Co., Ltd. make) of 30 weight sections was dissolved in the tetrahydrofuran solution (coal tar pitch: 30 weight sections, tetrahydrofuran:300 weight section) of the coal tar pitch which carried out filtration removal of the example 1 insoluble matter. Graphite particle 100 weight section was added in this solution, and it mixed in it, and stirring and mixing of were done, flowing back in the boiling point for 1 hour. What the pore volume of the range of 0.01-100 micrometers measured with the impurity content of 200 ppm and a method of mercury penetration combines the used graphite particles in 0.78cc/g, and a flat shape particle (0.3362 nm and not less than 100 nm) combines with non parallel mutually, respectively in d002 and Lc was used.

[0041]Subsequently, the tetrahydrofuran was removed using the rotary evaporator and vacuum drying was carried out at 100 ** for 3 hours. The complex which consists of an obtained partial condensation polymer of graphite particles, a coal tar pitch, and a tetramethoxy silane was cracked by the cutter mill,

and they could be 200 or less mesh. Among the air, the speed for 3 **/, to 250 **, temperature up of the obtained complex powder was carried out, and it was held for 1 hour. Subsequently, it held for 1 hour, and a coal tar pitch and tetramethoxy silane partial condensate were carbonized, it decomposed [temperature up was carried out to 1000 ** at 20 **/hour in speed among the nitrogen air current, and], and the graphite particles containing silicon and the complex which consists of amorphous carbon were obtained. This was cracked by the cutter mill and they could be 200 or less mesh.

[0042]When the silicon content was measured by X-ray fluorescence about the obtained compound carbon particle, it was 5.7 % of the weight. The mean particle diameter was 26 micrometers. The diffraction line of crystalline silicon content compounds, such as silicon carbide, was not observed in the wide angle X diffraction figure of the compound carbon particle. On the other hand, the diffraction line of low strength was accepted with the broadcloth of the diffraction line which has the strong sharp intensity of the carbon (002) side where it originates in graphite particles in any case, and the carbon (002) side resulting from amorphous carbon of coal tar pitch origin. The spacings d_{002} which were attached to these diffraction lines and measured were 0.3356 nm and 0.3471 nm, respectively. The specific surface area measured with the BET adsorption method using complex nitrogen was 1.5m²/g.

[0043]The compound carbon particle was produced like Example 1 except having made the example 2 tetramethoxy silane partial condensation polymer addition into 45 weight sections. The silicon content of the obtained complex powder was 9.8 % of the weight. The mean particle diameter was 27 micrometers. The diffraction line of crystalline silicon content compounds, such as silicon carbide, was not observed in the wide angle X diffraction figure of the compound carbon particle. The diffraction line of low strength was accepted with the broadcloth of the diffraction line which, on the other hand, has the strong sharp intensity of the carbon (002) side resulting from graphite particles, and the carbon (002) side resulting from amorphous carbon of coal tar pitch origin. The spacings d_{002} which were attached to these diffraction lines and measured were 0.3355 nm and 0.3472 nm, respectively. The specific surface area measured with the BET adsorption method using complex nitrogen was 1.8m²/g.

[0044]Complex powder was produced like Example 1 except having made the example 3 tetramethoxy silane partial condensation polymer addition into 63 weight sections. The silicon content of the obtained complex powder was 15.3 % of the weight. The mean particle diameter was 28 micrometers. The diffraction line of crystalline silicon content compounds, such as silicon carbide, was not observed in the wide angle X diffraction figure of the compound carbon particle. The diffraction line of low strength was accepted with the broadcloth of the diffraction line which, on the other hand, has the strong sharp intensity of the carbon (002) side resulting from graphite particles, and the carbon (002) side resulting from carbon of coal tar pitch origin. The spacings d_{002} which were attached to these diffraction lines and measured were 0.3362 nm and 0.3453 nm, respectively. The specific surface area measured with the BET adsorption method using complex nitrogen was 2.5m²/g.

[0045]The outside which does not add a comparative example 1 tetramethoxy silane partial condensation polymer produced complex powder like Example 1. The spacings d_{002} which were attached to the diffraction line of low strength and measured with the broadcloth of the diffraction line which has the strong sharp intensity of the carbon (002) side resulting from graphite particles, and the carbon (002) side resulting from amorphous carbon of coal tar pitch origin were 0.3355 nm and 0.3468 nm, respectively. The specific surface area measured with the BET adsorption method using complex nitrogen was 1.1m²/g.

[0046]Among the air, the speed for 3 **/, to 250 **, temperature up of the complex powder which

consists of a partial condensation polymer of graphite particles, a coal tar pitch, and a tetramethoxy silane produced like four to example 6 Example 1 was carried out, and it was held for 1 hour. Subsequently, it held for 1 hour, and a coal tar pitch and tetramethoxy silane partial condensate were carbonized, it decomposed [temperature up was carried out at 20 **/hour in speed among the nitrogen air current to the prescribed temperature up to 900 **, 1000 **, and 1400 **, and], and the graphite particles containing silicon and the complex which consists of amorphous carbon were obtained. This was cracked by the cutter mill and they could be 200 or less mesh. The mean particle diameter of the obtained particles was 27 micrometers (900 **), 27 micrometers (1000 **), and 23 micrometers (1400 **).

[0047]About the obtained complex powder, the silicon content was measured by X-ray fluorescence. The result is shown in Table 1. The diffraction line of crystalline silicon content compounds, such as silicon carbide, was not observed in the wide angle X diffraction figure of these complex powder. On the other hand, the diffraction line of low strength was accepted with the broadcloth of the diffraction line which has the strong sharp intensity of the carbon (002) side where it originates in graphite particles in any case, and the carbon (002) side resulting from carbon of coal tar pitch origin. The value of the spacing d002 which was attached to these diffraction lines and measured is shown in Table 1. The specific surface area of the obtained complex powder was measured using the BET adsorption method using nitrogen. The result is shown in Table 1.

[0048]

[Table 1]

表 1 物性及び充放電特性

試 料	炭素化温度 (℃)	珪素含有量 (重量%)	d 0 0 2 (nm)		比表面積 (m ² /g)	容 量 (初回) (Ah/kg)		
			黒鉛質粒子	炭素前駆体		充 電	放 電	不可逆
実施例 1	1 0 0 0	5 . 7	0 . 3 3 5 6	0 . 3 4 7 1	1 . 5	4 1 5	3 7 0	4 5
実施例 2	1 0 0 0	9 . 8	0 . 3 3 5 5	0 . 3 4 7 2	1 . 8	4 5 0	3 9 5	5 5
実施例 3	1 0 0 0	1 5 . 3	0 . 3 3 5 4	0 . 3 4 7 4	2 . 5	5 0 5	4 3 0	7 5
比較例 1	1 0 0 0	0 . 0 3	0 . 3 3 5 5	0 . 3 4 6 8	1 . 1	3 7 0	3 4 5	2 5
実施例 4	9 0 0	8 . 6	0 . 3 3 5 6	0 . 3 4 7 5	1 . 8	4 5 0	3 8 5	6 5
実施例 5	1 0 0 0	8 . 5	0 . 3 3 5 6	0 . 3 4 7 1	1 . 8	4 4 3	3 8 8	5 5
実施例 6	1 4 0 0	8 . 0	0 . 3 3 5 5	0 . 3 4 6 5	3 . 8	4 3 0	3 9 5	7 5

[0049](Charge-and-discharge volumetry) To 90 % of the weight of obtained complex powder, the polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone was added and kneaded 10% of the weight by solid content, and the slurry was produced. This slurry was applied to 10-micrometer-thick rolled copper foil, and also it dried, and was considered as the negative electrode. Constant current charge and discharge according the produced sample electrode to 3 terminal method were performed, and evaluation as a rechargeable lithium-ion battery negative electrode was performed.

[0050]Drawing 1 is a schematic diagram of the rechargeable lithium-ion battery used for the experiment. The solution which dissolved LiPF_6 in the glass cell 1 as the electrolysis solution 2 so that it might become the concentration of 1 mol/l. at the constant volume mixed solvent of ethylene carbonate and a dimethyl carbo mate as shown in drawing 1 is put in, The sample electrode (negative electrode) 3, the separator 4, and the counter electrode (anode) 5 have been laminated and arranged, the reference electrode 6 was further hung from the upper part, and the rechargeable lithium-ion battery was produced. Metal lithium was used for the counter electrode and the reference pole, and the polyethylene fine porous film was used for the separator. It charged to 1.5V (V vs Li/Li⁺) by the constant current of 0.28 mA/cm², and the examination discharged to 0V (V vs Li/Li⁺) was done. The value of the charge-and-discharge capacity at the time of the first time charge and discharge measured by Table 1 and irreversible capacity is shown.

[0051](Production of a rechargeable lithium-ion battery) The partial section front view of an example of a cylindrical rechargeable lithium-ion battery is shown in drawing 2. in drawing 2 -- 7 -- an anode and 8 -- as for a negative electrode tab and 12, a separator and 10 are [a battery can and 14] gaskets an anode lid and 13 a positive electrode tab and 11 a negative electrode and 9. The rechargeable lithium-ion battery shown in drawing 2 was produced as follows.

[0052](Production of an anode) As positive active material, to LiCoO_2 288 weight section, polyvinylidene fluoride 5 weight section was added as a binder, and N-methyl-2-pyrrolidone was added to this, it mixed with scaly-natural-graphite 7 weight section whose mean particle diameter is 1 micrometer as a conducting agent, and the slurry of positive electrode mixture was prepared to it. Subsequently, by having used this positive electrode mixture as the positive pole collector, it applied to both sides, dried, ranked second to aluminium foil (25 micrometers in thickness) with the doctor blade method, and pressing of the electrode was carried out with the roller press. This was produced at 40 mm in width, and the anode 10 was produced by logging in a size 285 mm in length. However, positive electrode mixture was not applied, but aluminium foil was exposed, and the portion with a length of 10 mm of the both ends of the anode 10 stuck the positive electrode tab 13 to one of these by pressure by ultrasonic jointing.

[0053](Production of a negative electrode) A sample expanded graphite grinding thing and a carbon complex, and the polyvinylidene fluoride as a binder are mixed by the ratio of the weight ratio 90:10, using both sides of copper foil (10 micrometers in thickness) as a negative pole collector with ** with a doctor blade method, after making a solvent (N-methyl-2-pyrrolidone) distribute this and considering it as a slurry -- desiccation -- subsequently pressing of the electrode was carried out with the roller press. This was produced at 40 mm in width, and the negative electrode was produced by logging in a size 290 mm in length. The negative electrode tab was stuck to one side of the portion by which this negative electrode is not applied to the negative electrode mixture of a portion with a length of 10 mm of both ends as well as an anode by pressure by ultrasonic jointing.

[0054](Preparation of an electrolysis solution) 1 mol/l. of LiPF_6 was dissolved in the constant volume mixed solvent of ethylene carbonate and dimethyl carbonate, and the electrolysis solution was prepared.

[0055](Production of a cell) After laminating said anode, the separator which consists of a porosity film made from polyethylene (25 micrometers in thickness, and 44 mm in width), and said negative electrode in this order, it wound spirally and the electrode group was produced so that said negative electrode

might be located outside. This electrode group was stored to the battery can made from stainless steel, can bottom welding of the negative electrode tab was carried out, and the converging section for closing an anode lid was formed. Then, said electrolysis solution was poured into the battery can, the positive electrode tab was welded to the anode lid, and the cylindrical rechargeable lithium-ion battery was produced for the anode lid in total. The charge and discharge current was 200 mA, and the charge-discharge cycle characteristic of each cell was measured. The result is shown in Table 2.

[0056]

[Table 2]

表 2 サイクル特性

試 料	容量維持率 (300サイクル目)
実施例 1	93
実施例 2	92
実施例 3	90
比較例 1	94
実施例 4	90
実施例 5	93
実施例 6	94

[0057]

[Effect of the Invention]The compound carbon particle of this invention with low reactivity with the high charge-and-discharge capacity of high graphite carbon, and an electrolysis solution. The feature arborescence metal lithium is hard to generate that discharge voltage is high and flat is maintained, and it excels in a cycle characteristic, and is suitable as a negative pole material for lithium secondary batteries with small irreversible capacity.

[0058]According to the manufacturing method of the compound carbon particle of this invention, the high charge-and-discharge capacity of high graphite carbon, The feature arborescence metal lithium with low reactivity with an electrolysis solution is hard to generate that discharge voltage is high and flat is maintained, it excels in a cycle characteristic, and a compound carbon particle suitable as a negative pole material for lithium secondary batteries with small irreversible capacity is obtained.

[0059]The negative pole material of this invention is suitable for the lithium secondary batteries with small irreversible capacity which maintained the feature arborescence metal lithium with low reactivity with the high charge-and-discharge capacity of high graphite carbon and an electrolysis solution is hard to generate that discharge voltage is high and flat, and were excellent in the cycle characteristic.

[0060]The irreversible capacity of the negative electrode for lithium secondary batteries of this invention which has the feature arborescence metal lithium with low reactivity with high charge-and-discharge capacity and an electrolysis solution is hard to generate that discharge voltage is high and flat, and was excellent in the cycle characteristic is small. The lithium secondary battery of this invention has high service capacity, and is excellent in a cycle characteristic, and its irreversible capacity is small.

[Translation done.]

